

Effect of Carbonation on Autogenous Self-healing in Cementitious Materials

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ABSTRACT

It has been reported that autogenous self-healing in cementitious materials can only take place when water is present in cracks. When cracks in concrete are filled with water, CO₂ from the atmosphere dissolves into the water and diffuses into cracks. CO₃²⁻ ions can only diffuse into the crack very slowly through the crack mouth. In this case, reaction products of further reaction of reactive materials, i.e. unhydrated cement and blast furnace slag, can be formed in cracks firstly. As CO₃²⁻ ions diffuse into the crack gradually, or when the cracks become dry and exposed to atmosphere directly, the newly formed reaction products in the cracks will be carbonated. However, the effect of carbonation process on the effect of autogenous self-healing of cracks is still not clear yet.

In this study, the effect of carbonation on self-healing is investigated by thermodynamic modeling. By using thermodynamic modeling, the transformation of phases and the corresponding volume change due to carbonation can be determined. It is found that in the cracks in Portland cement paste, the portlandite formed in the healing process is first transformed into calcite, followed by the carbonation of C-S-H forming calcite and silica gel. Because the carbonation of portlandite increases its volume, the filling fraction of cracks in Portland cement paste is improved by carbonation. In slag cement paste, carbonation of reaction products formed in cracks has a positive effect on the filling of cracks in the beginning of carbonation processes, but has negative effects later on. The change of the filling fraction of crack caused by carbonation depends on the mineralogy of the solids that had formed in cracks before the carbonation process.

1. INTRODUCTION

It has been reported that autogenous self-healing in cementitious materials can only take place when water is present in cracks. When cracks in concrete are filled with water, CO₂ from the atmosphere dissolves into the water and diffuses into cracks. CO₃²⁻ ions can only diffuse into the crack very slowly through the crack mouth. In this case, reaction products of further reaction of reactive materials i.e. unhydrated cement and blast furnace slag, can be formed in cracks firstly. As CO₃²⁻ ions diffuse into the crack gradually, or when the cracks become dry and exposed to atmosphere

directly, the newly formed reaction products in the cracks will be carbonated. However, the effect of carbonation process on the effect of autogenous self-healing of cracks is still not clear yet. In this study, the effect of carbonation on self-healing is investigated by thermodynamic modeling. By using thermodynamic modeling, the transformation of phases and the corresponding volume change due to carbonation can be determined.

2. MATERIALS

The materials used in this study are Portland cement paste and slag cement paste. CEM I 42.5N is used to prepare Portland cement paste, while CEM III/B 42.5N is used to prepare slag cement paste. Their chemical compositions are presented in Table 1 and 2, respectively. In CEM III/B 42.5N, clinker accounts for 34.1% by mass. The water to cement ratio (w/c) of the cement paste is 0.3.

Table 1: Chemical composition of CEM I 42.5N.

Compound	CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	K ₂ O	Na ₂ O	SO ₃	MgO	Total
Weight (%)	64.40	20.36	4.96	3.17	0.64	0.14	2.57	2.09	98.33

Table 2: Chemical composition of CEM III/B 42.5N and the included slag (slag content: 66%).

Compound	CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	K ₂ O	Na ₂ O	SO ₃	MgO	Total
CEM III/B 42.5N (g/100 g cement)	45.52	30.61	10.58	1.42	0.6	0.31	2.66	7.33	99.01
Slag (g/100 g slag)	40.35	32.54	12.93	0.22	0.4	-	-	10.41	96.84

3. METHODS

The chemical reactions of autogenous self-healing both in Portland cement paste and slag cement paste are simulated by a geo-chemical model JCHESS [1]. The chemical reactions and the corresponding equilibrium constants for autogenous self-healing are implemented into the database of JCHESS. Detailed information of the simulation can be seen in [2, 3]. According to the simulations in [3], before carbonation the reaction products formed in cracks in Portland cement paste mainly consist of portlandite and C-S-H. In slag cement paste, the reaction products in cracks are mainly composed of C-S-H, C₃AH₆, ettringite and OH-hydrotalcite. By using thermodynamic modeling, the transformation of phases and the corresponding volume change due to carbonation can be determined. In this study, the degree of carbonation is defined as: $a_{car} = m_c / m_{c,t} \times 100\%$, where $m_{c,t}$ is the total mass of CO₂ needed for complete carbonation of the solids formed in the crack; m_c is the mass of CO₂ consumed by the carbonation of the solids at a certain stage.

4. RESULTS AND DISCUSSION

As reported in [3], after cracked Portland cement paste is immersed in water at the age of 28 days for 200 hours, the filling fraction of a crack with a width of 10 μm is about 36%: 32% with Portlandite and 4% with C-S-H. If these reaction products in

cracks are exposed to air, carbonation takes place. Figure 1 shows the transformation of reaction products in cracks and the corresponding change of the filling fraction of crack due to carbonation of the reaction products. Portlandite is carbonated first and transforms into calcite. The filling fraction of cracks increases during this process. When all the portlandite is reacted, C-S-H starts to be carbonated as well. Silica gel is formed and the filling fraction of cracks decreases slightly. When all the reaction products in cracks are carbonated, the filling fraction of cracks is increased by about 4% (in absolute sense). This is because the volume of portlandite, which is the main mineral of the reaction products in the crack, increases after the carbonation. This explains why self-healing proceeds faster when Portland cement paste is exposed to wet-dry cycles instead of submerged in water.

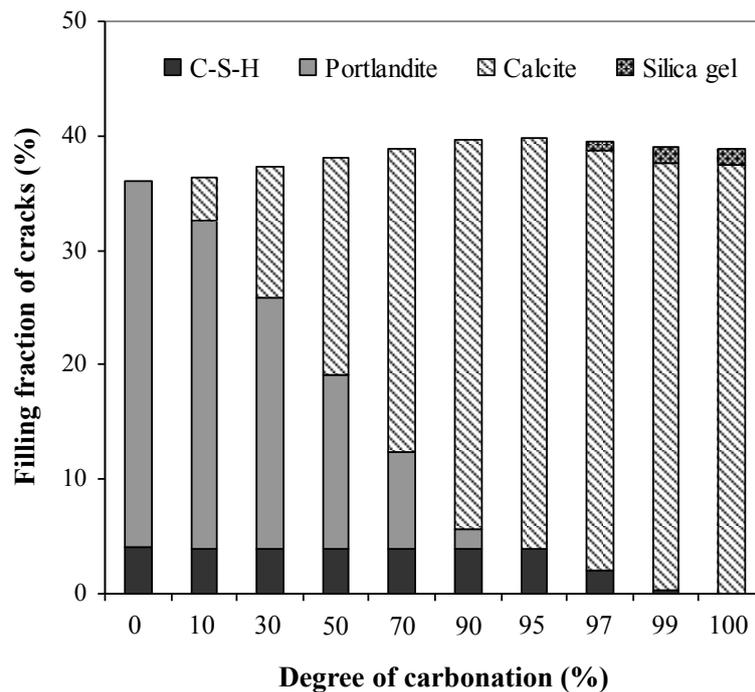


Figure 1: Transformation of reaction products formed in cracks in Portland cement paste due to carbonation. Initial composition of reaction products: 32% portlandite and 4% C-S-H.

For the case of slag cement paste, in the beginning of the carbonation process, first C_3AH_6 transforms into monocarboaluminate. Simultaneously, C_2ASH_8 is formed, of which Si originates from C-S-H (see Figure 2). If carbonation continues, the amounts of monocarboaluminate and C-S-H decrease, whereas the amount of C_2ASH_8 increases. In this process, calcite is formed and its amount increases gradually. The total volume of all the solids slightly increases. Once all the monocarboaluminate is consumed and transformed into calcite and C_2ASH_8 , silica gel is formed. The amount of C-S-H decreases continuously, while the amounts of silica gel and calcite increase. The amount of C_2ASH_8 remains constant. In this process, the total volume of all the solids decreases. After all the C-S-H has reacted, the carbonation of C_2ASH_8 starts and gibbsite is formed. As the volume of C_2ASH_8 decreases, the volumes of silica and gibbsite increase. At this stage, the total volume of solid phases slightly decreases. From Figure 2, it can be learned that carbonation of reaction products formed in an artificial crack has a positive effect on the efficiency of self-healing in the beginning, but has negative effects later on. When the solids in the

crack are carbonated completely, the filling fraction of cracks decreases by approximately 13%. This is different from the case of Portland cement paste, which is caused by the different mineralogy of the solid phases formed in the crack.

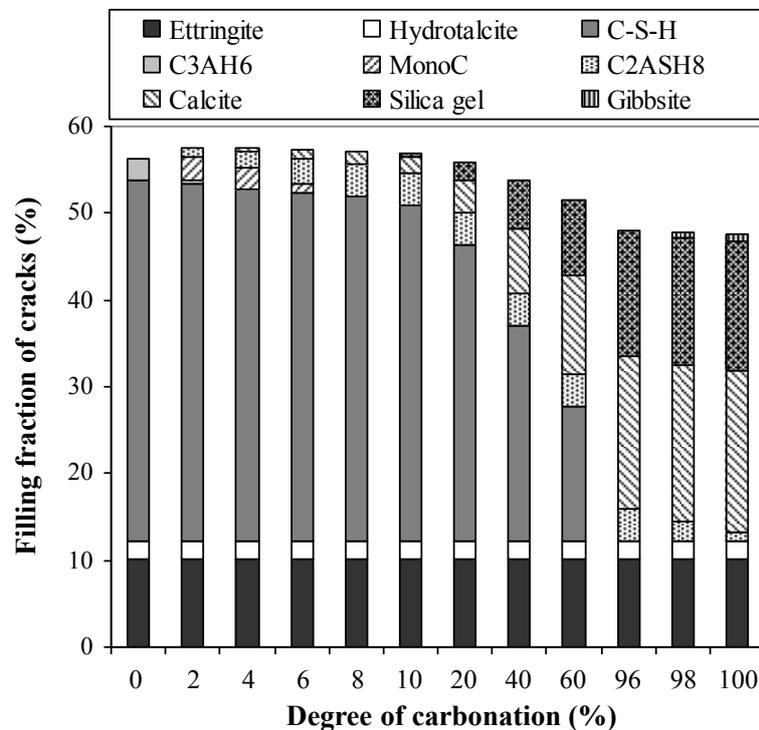


Figure 2: Transformation of the reaction products formed in cracks in slag cement paste due to carbonation. Initial composition of reaction products: 41% C-S-H, 10% ettringite, 3% hydrotalcite and 3% C₃AH₆.

5. CONCLUSIONS

Filling fraction of crack due to self-healing increases after carbonation in Portland cement paste, while decreases in slag cement paste. The change of the filling fraction of crack caused by carbonation depends on the mineralogy of the solids that had formed in cracks before the carbonation process.

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